

PATENT SPECIFICATION

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NO DRAWINGS.

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COMPLETE SPECIFICATION.

Polymerisation Catalysts.

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we
5 pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement :—

This invention relates to polymerisation
10 catalysts.

According to the present invention polymerisation catalysts may be prepared by treating a compound of a transition metal of Groups 4 to 6 of the Periodic System as
15 hereinafter defined with a compound of the formula $R_1R_2AlAOR_3$ where R_1 , R_2 and R_3 are alkyl, cycloalkyl, aryl or aralkyl hydrocarbon groups and A is a divalent aromatic hydrocarbon radical. The said transition
20 metals are metals occupying any of the 4th to 6th places after the inert gases in one of the long periods of the periodic system of elements, it being understood that the rare earths occupy only one place in the periodic
25 system, that is, a third place after an inert gas. In this Specification (including the claims) such metals are referred to as "transition metals of Groups 4 to 6 of the Periodic System." It is believed that the
30 catalysts produced as a result of the process of our invention are produced as a result of chemical reaction between components treated with one another.

Compounds of the formula $R_1R_2AlAOR_3$ may be prepared by reacting a compound
35 having the formula R_1R_2AlX with a compound having the formula $MAOR_3$, R_1 , R_2 and R_3 having the meaning previously assigned to them, X being a halogen atom and M is an alkali metal. For the most
40

active catalysts of this invention R_1 and R_2 are preferably alkyl and for economy in our catalysts R_1 , R_2 and R_3 are preferably ethyl groups. Thus, $(CH_3CH_2)_2Al.C_6H_4.O.CH_2CH_3$ can be prepared by reacting $(CH_3CH_2)_2AlCl$ with $Li.C_6H_4.O.CH_2CH_3$, e.g. in a molar ratio of 1:1. 45

Our preferred compounds of transition metals of Groups 4 to 6 of the Periodic System are halides, particularly chlorides, and we find that the process of this invention is most easily conducted when these compounds are compounds of titanium or vanadium, the choice of compound depending upon the nature of the polymer which it is desired to produce. The catalysts of this invention are particularly useful for polymerising purely hydrocarbon monomers; and 50

To polymerise ethylene to solid polymers $TiCl_4$ is our preferred transition metal compound because of its activity, relative availability and the ease with which it may be handled, as it is both volatile and soluble in petroleum ether; 60

To polymerise propylene to an isotactic polymer a trivalent titanium chloride is preferred as when used in the forms in which it is normally produced, the catalysts of this invention result in highly crystalline polypropylene. (We particularly prefer to use the chloride of trivalent titanium obtained by reacting $TiCl_4$ with aluminium according to our copending Application No. 39342/56 (Serial No. 877,050) since highly crystalline polypropylenes of very high isotactic content are thereby obtained.) 65 70 75

(The highly active form of $TiCl_3$ obtained by reacting $TiCl_4$ with aluminium may be conveniently prepared by heating aluminium, aluminium chloride and excess of titanium 80

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Price 2s. 7d.

tetrachloride together at temperatures up to about 250° C., if desired in the presence of an inert diluent, e.g. a liquid hydrocarbon, and then removing the unreacted titanium tetrachloride.)

To polymerise styrene to isotactic polystyrene VCl_4 is preferred because of the good yields of this polymer which result from its use;

To polymerise butadiene to a rubbery polymer we choose TiCl_3 but if a crystalline polymer is required we choose VCl_4 ;

To polymerise isoprene to a rubbery polymer we choose TiCl_3 but if a crystalline polymer is required we choose VCl_4 .

We find that the ratio in which the aluminium compound and the transition metal compound are reacted together has an important effect upon the molecular weight of polymer produced using the catalysts of this invention or an important effect on the nature of the polymer so produced. We find that catalysts which result in the most valuable polymer, either with respect to its molecular weight or with respect to its chemical configuration are obtained when the mole ratio (equivalent to the ratio of moles of aluminium compound to gram atoms of Ti in the aforementioned trivalent titanium chloride when this latter is used) of aluminium compound to transition metal compound used in the process of this invention is between 0.1 : 1 and 10 : 1.

The process of this invention is preferably conducted in the presence of a hydrocarbon liquid as the best yields are thereby obtained. Conveniently, such hydrocarbon liquid may be an aliphatic hydrocarbon liquid. However, as the said compounds of formula $\text{R}_1\text{R}_2\text{AlAOR}_2$ are not very soluble in aliphatic hydrocarbon liquids, it is convenient to use sufficient aromatic hydrocarbon liquid e.g. benzene to keep them in solution in the hydrocarbon liquid. Such a liquid is preferably one which is free from sulphur containing constituents as these poison the catalyst. It will be appreciated that the reaction of this invention may often be conducted in the presence of monomer as solvent (or in the case of ethylene under high pressure as dispersion medium). Thus the aluminium compound and the transition metal compound may be dissolved (or dispersed) in the monomer and the two solutions mixed together. Similarly, the aluminium compound may be dissolved (or dispersed) in the monomer and the transition metal compound added to this solution (or dispersion), e.g. in the case of TiCl_3 or VCl_4 in the form of vapour. It will also be appreciated that, if the catalysts resulting from this invention are used in polymerisation reactions of liquid or gaseous monomers and the reactions are not taken to completion, the monomer not polymerised can be regarded as solvent (or

dispersion medium) for the polymerisation reaction. It will further be appreciated that many of the transition metal compounds suitable for use in the process of this invention are not soluble in hydrocarbon solvents. Important examples of such compounds are TiCl_3 and the aforementioned trivalent titanium chloride obtained by reacting TiCl_4 with aluminium. When such compounds are used in the process of this invention it is preferable to mill them e.g. by ball milling them, as the most active catalysts are thereby obtained. When TiCl_3 or the aforementioned trivalent titanium chloride is so milled it is preferred that the size of the TiCl_3 particles is not reduced to colloidal sizes, as the particularly useful effects obtained by TiCl_3 are thereby destroyed.

As the aluminium compounds used in and the catalyst produced by the process of this invention are decomposed by oxygen or humidity, the process of this invention and polymerisations using the catalysts produced should be conducted in the absence of air or moisture or in the presence of only limited amounts of them.

In view of the reactive nature and colour of the catalysts of our invention it is desirable to remove these catalysts from polymeric materials produced with them. The catalysts may be decomposed by treating polymeric materials containing them with a hydroxyl containing compound, e.g. water or steam, or an alcohol, including a dry alcohol, e.g. methanol or butanol. The decomposition products may then be removed by washing the polymeric materials with for example methanol, an acid or alkaline medium as is appropriate.

The following examples further illustrate our invention but it will be understood that our invention is in no way limited by these examples.

EXAMPLE 1.

10 g. aluminium powder and 10 g. freshly sublimed aluminium chloride were added to 500 cc. titanium tetrachloride under an atmosphere of nitrogen. The mixture was stirred and the temperature gradually raised to about 130° C. when a vigorous reaction commenced. Heating was then discontinued until the rate of reaction moderated; the reaction mixture was then heated under reflux conditions for 17 hours. The excess of titanium tetrachloride together with free aluminium trichloride was then distilled off at atmospheric pressure and the residual solid heated at 200° C. under 0.2 mm. Hg. absolute pressure for 5 hours to remove any remaining titanium tetrachloride. 174 g. of a pale purple solid showing an X-ray diffraction pattern were obtained.

1.6 g. of the above purple solid (containing 0.008 gram-atoms of titanium) was ball milled in petroleum ether (40 ml., b.p. 130

120° C.) for 20 hours. The suspension was transferred to a small autoclave (200 ml. capacity) using further petroleum ether (25 ml.) as washings. A solution of *p*-ethoxy phenyl aluminium diethyl (0.019 moles), prepared as described below, in benzene (20 ml.) were added, then propylene (36 g., 70 ml.). On heating to 65° C. there was a rapid exothermic reaction during which the pressure in the autoclave rose to a maximum of 250 p.s.i. The reaction was complete in twenty minutes. After addition of methanol, the polypropylene was isolated by filtration and extraction with methanol and dried. The yield of polypropylene was 27 g. of which 82% was insoluble in ether.

EXAMPLE 2.

TiCl₃ (1.75 g., 0.01135 moles) was ball milled in petroleum ether (40 ml., b.p. 120° C.) for 14 hours. The suspension was transferred to a small autoclave (200 ml. capacity) using an addition of 20 ml. of petroleum ether as washings. A solution of *p*-ethoxy phenyl aluminium diethyl (2.114 g., .0066 moles) prepared as described below in petroleum ether (b.p. 120° C., 20 ml.) and benzene (10 ml.) and then propylene (36 g., 70 ml.) were added. On heating the autoclave to 80° C. a vigorous exothermic reaction took place, the temperature rising to 140° C. The autoclave was then cooled and methanol added. The polypropylene was isolated by filtration and extraction with methanol and then dried. The yield of polypropylene was 21.0 g. of which 77.4% was insoluble in ether.

Preparation of *p*-ethoxy phenyl aluminium diethyl.

Diethyl aluminium bromide (8.36 g., 0.0506 moles) in ether (50 ml.) was added to *p*-ethoxy phenyl lithium (0.0506 mole) in ether (185 ml.) with shaking and was then kept at ambient temperature overnight. The ether was removed at 10 mm/Hg. pressure and replaced by benzene (150 ml.). The lithium bromide formed, together with the lithium bromide present in the ether solution of *p*-ethoxy phenyl lithium as a result of the preparation thereof, was filtered off and amounted to 9.79 g. (theoretical quantity = 9.76 g.). The benzene was distilled off and the residue kept at 0.03 mm/Hg. overnight. The product (13.9 g.) was a pale yellow viscous oil, probably containing ether as the etherate.

WHAT WE CLAIM IS:—

1. A composition suitable for catalysing the polymerisation of ethylene or vinyl hydrocarbons obtained by treating a com-

pound of a transition metal of Groups 4 to 6 of the Periodic System as hereinbefore defined with a compound of the formula $R_1R_2AlAOR_3$ where R_1 , R_2 and R_3 are alkyl, cycloalkyl, aryl or aralkyl hydrocarbon groups and A is a divalent aromatic hydrocarbon radical.

2. A composition as claimed in Claim 1 in which a compound of formula $R_1R_2AlAOR_3$ is prepared by reacting a compound having the formula R_1R_2AlX with a compound having the formula $MAOR_3$ in which X is a halogen atom and M is an alkali metal atom.

3. A composition as claimed in Claim 2 in which a compound having the formula R_1R_2AlX and the compound having the formula $MAOR_3$ are added to each other substantially in a molar ratio of 1 : 1.

4. A composition as claimed in any of the preceding claims in which the compound of a transition metal is a halide, preferably a chloride.

5. A composition as claimed in any of the preceding claims in which the transition metal is either titanium or vanadium.

6. A composition as claimed in any of the preceding claims in which the mole ratio of the aluminium compound of the transition metal compound is between 0.1:1 and 10:1.

7. A composition as claimed in any of the preceding claims whenever prepared in the presence of hydrocarbon liquid, preferably an aromatic hydrocarbon liquid.

8. A composition as claimed in Claim 7 in which the hydrocarbon is free from sulphur containing constituents.

9. A composition as claimed in any of the preceding claims in which a solid compound of a transition metal is subjected to milling, preferably ball milling, in which the particles are not reduced to colloidal sizes.

10. A composition as claimed in any of Claims 1 to 8 in which the compound of a transition metal is TiCl₄.

11. A composition as claimed in any of Claims 1 to 9 in which the compound of a transition metal is a trivalent titanium chloride.

12. A composition as claimed in any of Claims 1 to 8 in which the compound of a transition metal is VCl₄.

13. A composition as claimed in Claim 1 and substantially as hereinbefore described with particular reference to the examples.

14. A process of polymerising a hydrocarbon monomer in which the monomer is contacted with any composition claimed in any of the preceding claims.

15. A process for the polymerisation of propylene to isotactic polypropylene in which propylene is brought into contact with a composition as claimed in Claim 11.

16. A process for the polymerisation of propylene as claimed in Claim 15 and sub-

stantially as hereinbefore described with particular reference to the examples.

17. Polypropylene whenever produced by a process as claimed in any of Claims 14 to 16.

ALFRED O. BALL,
Agent for the Applicants.

PROVISIONAL SPECIFICATION.

Polymerisation Catalysts.

- 5 We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare this invention to be described in the following statement:—
- 10 This invention relates to polymerisation catalysts.
- According to the present invention polymerisation catalysts may be prepared by treating a compound of a transition metal as hereinafter defined with a compound of the
- 15 formula $R^1R^{11}AlAOR^{111}$ or $MR^1R^{11}Al(AOR^{111})_2$ where R^1 , R^{11} and R^{111} may be alkyl, cycloalkyl, aryl or aralkyl hydrocarbon groups, A is a divalent aromatic hydrocarbon radical and M is an alkali metal. The said transition metals are metals occupying any of the 4th to 10th places after the inert gases in one of the long periods of the periodic system of elements, it being
- 20 understood that the rare earths occupy only one place in the Periodic System, that is, a third place after an inert gas. It is believed that the catalysts produced as a result of the process of our invention are produced as a
- 25 result of chemical reaction between components treated with one another.
- Compounds of the formula $R^1R^{11}AlAOR^{111}$ or $MR^1R^{11}Al(AOR^{111})_2$ may be prepared by reacting a compound having the formula
- 30 $R^1R^{11}AlX$ with a compound having the formula $MAOR^{111}$, R^1 , R^{11} , R^{111} and M having the meaning previously assigned to them and X being a halogen atom. For the most active catalysts of this invention R^1 and R^{11} are preferably alkyl and for economy in
- 35 our catalysts R^1 , R^{11} and R^{111} are preferably ethyl groups. Thus, $(CH_3CH_2)_2AlC_6H_4OCH_2CH_3$ can be prepared by reacting one mole of $(CH_3CH_2)_2AlCl$ with one mole of $LiC_6H_4OCH_2CH_3$, and $Li(CH_3CH_2)_2Al(C_6H_5OCH_2CH_3)_2$ can be prepared by reacting one mole of $(CH_3CH_2)_2AlCl$ with
- 40 two moles of $LiC_6H_4OCH_2CH_3$.
- Our preferred transition metal compounds are halides, particularly chlorides, and we find that the process of this invention is most easily conducted when these compounds are
- 45 compounds of metals which occupy the 4th, 5th or 6th places after the inert gases in one of the long periods of the Periodic System and these compounds are preferably compounds of titanium or vanadium, the choice of compound depending upon the nature of the polymer which it is desired to produce.
- The catalysts of this invention are particularly useful for polymerising purely hydrocarbon monomers; and
- 60 To polymerise ethylene $TiCl_4$ is our preferred transition metal compound because of its activity, relative availability and the ease with which it may be handled, as it is both
- 65 volatile and soluble in petroleum ether;
- To polymerise propylene to an isotactic polymer $TiCl_3$ is preferred as when used in the forms in which it is normally produced, the catalysts of this invention result in
- 70 highly crystalline polypropylene;
- To polymerise styrene to isotactic polystyrene VCl_4 is preferred because of the good yields of this polymer which result from its
- 75 use;
- To polymerise butadiene to a rubbery polymer we choose $TiCl_3$ but if a crystalline polymer is required we choose VCl_4 ;
- 80 To polymerise isoprene to a rubbery polymer we choose $TiCl_4$ but if a crystalline polymer is required we choose VCl_4 .
- We find that the ratio in which the aluminium compound and the transition metal compound are reacted together has an important effect upon the molecular weight of polymer produced using the catalysts of this invention or an important effect on the nature
- 85 of the polymer so produced. We find that catalysts which result in the most valuable polymer, either with respect to its molecular weight or with respect to its chemical configuration, are obtained when the mol ratio of aluminium compound to transition metal
- 90 compound used in the process of this invention is one to one or thereabout.
- The process of this invention is preferably conducted in the presence of a hydrocarbon solvent. Such a solvent is preferably one which is free from sulphur or aromatic hydrocarbons as the catalyst is preferably used as a
- 95 polymerisation catalyst in the presence of the solvent in which it is produced and best polymerisation yields are obtained with aliphatic solvents free from sulphur or aromatic components. We find that normally when the more useful polymers are made using the catalysts of this invention the ratio of the amount of solvent used with the catalyst to the amount of monomer polymerised has an
- 100 effect on the yield of polymer produced and we prefer to use a ratio of solvent to monomer between 2:1 and 7:1, preferably between 2:1 and 4:1, parts by volume. It will be
- 105
- 110

5 appreciated that the reaction of this inven-
tion may often be conducted in the presence
of monomer as solvent (or in the case of
ethylene under high pressure as dispersion
medium). Thus the aluminium compound and
the transition metal compound may be dis-
solved (or dispersed) in the monomer and
the two solutions mixed together. Similarly,
10 the aluminium compound may be dissolved
(or dispersed) in the monomer and the
transition metal compound added to this
solution (or dispersion), e.g. in the case of
 TiCl_4 or VCl_4 in the form of vapour. It will
15 also be appreciated that, if the catalysts
resulting from this invention are used in
polymerisation reactions of liquid or gaseous
monomers and the reactions are not taken to
completion, the monomer not polymerised
20 can be regarded as solvent (or dispersion
medium) for the polymerisation reaction. It
will further be appreciated that many of the
transition metal compounds suitable for use
in the process of this invention are not
soluble in hydrocarbon solvents. An im-
25 portant example of such compounds is
 TiCl_3 . With such compounds the process of
this invention can be carried out by milling,
e.g. ball milling the ingredients together, the
aluminium compound being preferably dis-
30 solved in a hydrocarbon solvent. When the

process is conducted in this way it is pre-
ferred that the size of the TiCl_3 particles is not
reduced to colloidal sizes, as the particularly
useful effects obtained by TiCl_3 are thereby
destroyed.

35 As the aluminium compounds used in and
the catalyst produced by the process of this
invention are decomposed by oxygen or
humidity, the process of this invention and
polymerisations using the catalysts produced
40 should be conducted in the absence of air or
moisture or in the presence of only limited
amounts of them.

In view of the reactive nature and colour
of the catalysts of our invention it is desirable
45 to remove these catalysts from polymeric
materials produced with them. The catalysts
may be decomposed by treating polymeric
materials containing them with a hydroxyl
containing compound, e.g. water or steam,
50 or an alcohol, including a dry alcohol, e.g.
methanol or butanol. The decomposition
products may then be removed by washing
the polymeric materials with for example
methanol, an acid or alkaline medium as is
55 appropriate.

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